Novel, Trimeric Mn-Substituted Undecatungstosilicate, $[(\beta_2\text{-SiW}_{11}\text{MnO}_{38}\text{OH})_3]^{15-}$ [†]

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Introduction

Polyoxometalates are metal−oxygen cluster species with an enormous structural variety and interesting properties leading to applications in catalysis, medicine, magnetochemistry, and materials science.[1−4] In most cases synthesis of novel polyoxometalates is amazingly simple and straightforward, once the proper reaction conditions have been identified. However, the mechanism of formation of polyoxometalates is not well understood and is commonly described as self-assembly. Therefore systematic structural design and derivatization of novel polyoxometalates remains a challenge.

The chemistry of silicotungstates has been studied for many years and is in general quite well-known.[5] The monovacant $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ and the trivacant $[\text{A-x-SiW}_9\text{O}_{34}]^{10-}$ ($x = \alpha, \beta$) are typical examples of stable, lacunary silicotungstates. The three monolacunary isomers $[\beta_x\text{-SiW}_{11}\text{O}_{39}]^{8-}$ ($x = 1, 2, 3$) are examples of metastable silicotungstates which convert slowly in aqueous solution according to $[\beta_1\text{-SiW}_{11}\text{O}_{39}]^{8-} \rightarrow [\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-} \rightarrow [\beta_3\text{-SiW}_{11}\text{O}_{39}]^{8-} \rightarrow [\alpha\text{-SiW}_{11}\text{O}_{39}]$.[8−] All lacunary silicotungstates easily incorporate first-row transition metals resulting in general in monomeric polyoxoanions with the well-known Keggin structure.[6] Structural rearrangement (e.g., isomerization) of the silicotungstate framework during transition metal incorporation is usually not observed. For $[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Fe(H}_2\text{O)}]^{5-}$ Tézé et al. reported formation of a dimer with an Fe−O−Fe bridge as a result of deprotonation of the polyoxoanion.[7] Very recently Tézé et al. reported that interaction of $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ with Fe^{3+} ions can lead to the dimeric $[\{\alpha\text{-SiW}_{10}\text{O}_{37}\text{Fe}_2(\text{OH})_2\}_2]^{12-}$.[8]

Another example of a lacunary silicotungstate is the divacant, metastable decatungstosilicate, $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$, which was first reported by Teze et al.[9] Zhang et al. reacted this polyanion with Mn^{2+} and obtained a disubstituted product.[10] Wassermann et al. investigated the reactivity of Cr^{3+} with $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$, and they also obtained a disubstituted product in which the two Cr^{3+} ions were bridged by two acetate anions.[11] Recently Nozaki et al. reported a diiron-substituted $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$.[12] All products were monomeric with the γ-framework retained. Canny et al. studied the reaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with vanadium, and they identified a mixture of disubstituted, monomeric β-isomers based on multinuclear NMR spectroscopy.[13] Xin et al. reacted $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with phenyltin and they isolated a dimer, where two $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ units are connected via two phenyltin bridges.[14] Recently Kortz et al. showed that interaction of Ni^{2+} with $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ resulted in the dimeric $[\{\beta\text{-SiNi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2(\text{H}_2\text{O})\}_2]^{12-}$.[15] The formation of this heteropolyanion involved insertion, isomerization ($\gamma \rightarrow \beta$), and dimerization. Very recently Kortz et al. also reported that reaction of Cu^{2+}, Mn^{2+}, and Zn^{2+} with $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ resulted in the dimeric, sandwich-type $[\{\text{SiM}_2\text{W}_9\text{O}_{34}(\text{H}_2\text{O})\}_2]^{12-}$ ($\text{M} = \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$).[16,17] In this case the reaction mechanism must have included insertion, isomerization ($\gamma \rightarrow \alpha$), dimerization, and loss of tungsten. This work shows that interaction of Mn^{2+} with $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ can lead to yet another unexpected manganese-substituted silicotungstate.

Experimental Section

A 2.23 g (0.75 mmol) sample of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (synthesized according to Tézé[9]) was added with stirring to a solution of 0.36 g (2.25 mmol) of $\text{MnCl}_2\cdot 2\text{H}_2\text{O}$ in 100 mL of H_2O. Then glacial acetic acid was added dropwise until pH 3.9. This solution was stirred at room temperature for 15 min. Addition of 10 g of solid CsCl led to a yellow precipitate, which was collected in a sintered-glass frit and air-dried. Layering of the above solution with a dilute solution of CsCl resulted in orange crystals suitable for X-ray crystallography after several days. Elemental analysis for a number of different samples prepared by the same procedure indicated that **1** was present in all cases, but that the Cs:K ratio in the crystalline solid varied significantly. The sample used for elemental analysis was from a different batch than the crystal used for X-ray analysis. IR: 997, 948, 893, 866, 814, 788, 736, 605, 553, 532 cm^{-1}. Anal. Calcd (found) for $\text{Cs}_4\text{K}_{11}[(\beta_2\text{-SiW}_{11}\text{MnO}_{38}\text{OH})_3]\cdot 27\text{H}_2\text{O}$: Cs, 5.52 (5.82); K, 4.46 (4.80); W, 62.94 (62.50); Mn, 1.71 (1.74); Si, 0.87 (1.15). Elemental analysis was performed by the Service Central d'Analyse of CNRS at 69390 Vernaison, France.

A yellow, column-shaped crystal with dimensions $0.50 \times 0.06 \times 0.06$ mm^3 was mounted on a glass fiber for indexing and intensity data collection at 173 K on a Siemens Smart-CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve the structure and to locate all heavy atoms (SHELXS86). Then the remaining atoms were found from successive difference maps (SHELXL93). It became apparent that a manganese atom was

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[†] This article is dedicated to Professor André Tézé (Université de Versailles) on the occasion of his retirement.

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(17) Our group has also been able to synthesize and isolate the Co^{2+} derivative of this series, $[\{\text{SiCo}_2\text{W}_9\text{O}_{34}(\text{H}_2\text{O})\}_2]^{12-}$, as based on IR spectroscopy.

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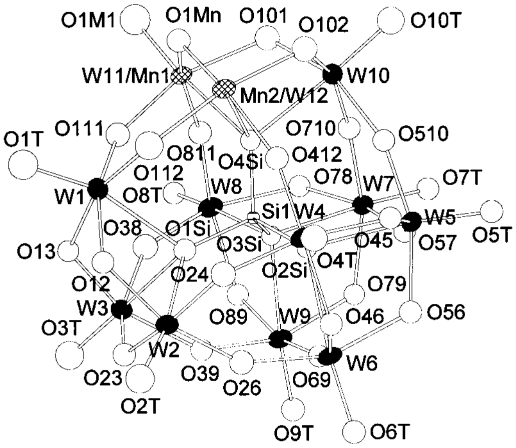

Figure 1. Ball and stick representation of the asymmetric unit of $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{15-}$ (**1**) showing 50% probability ellipsoids and the labeling scheme.

Table 1. Crystallographic Data for $CsK_{14}[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]\cdot 39H_2O$

empirical formula	$Cs_{0.33}K_{4.67}MnO_{52}SiW_{11}$
fw	3164.2
space group (No.)	*P*63 (173)
unit cell dimens	$a = b = 26.744(2)$ Å $c = 12.1309(15)$ Å
vol	$V = 7513.8(13)$ Å^3
Z	6
temp	−100 °C
wavelength	0.71073 Å
density (calcd)	4.196 Mg m^{-3}
abs coeff	26.153 mm^{-1}
$R(F_o)^a$	0.050
$R_w(F_o)^b$	0.126

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

disordered over two edge-shared, heavy atom sites adjacent to the rotated triad of the β-Keggin unit in the asymmetric unit (see Figure 1). It was possible to resolve the manganese disorder through assignment of partial Mn/W occupancies, which resulted in a significant drop of the *R* value. The best result for the single crystal studied was obtained for Mn/W occupancies of 0.6/0.4 and 0.4/0.6, respectively. The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (metal atoms), and isotropic thermal parameters (oxygen, silicon) converged at $R = 0.050$ and $R_w = 0.126$ ($I > 2\sigma(I)$). In the final difference map the deepest hole was −3.937 e Å^{-3} and the highest peak 3.967 e Å^{-3}. An absorption correction was performed using the SADABS program.[18] Crystallographic data are summarized in Table 1.

Discussion

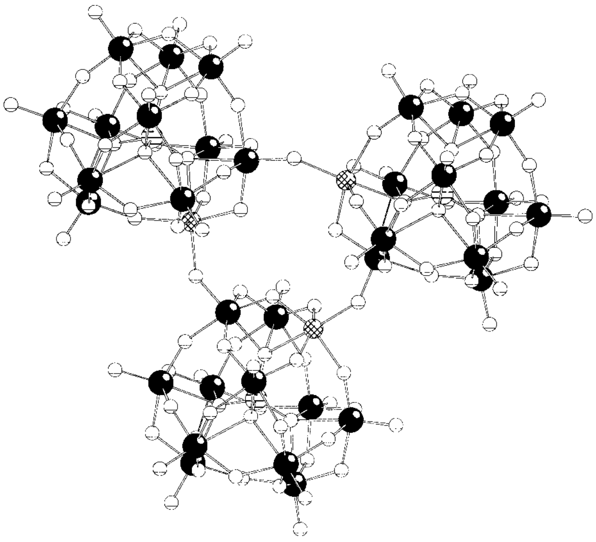

Figure 2. Ball and stick representation of one enantiomer of $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{15-}$ (**1**).

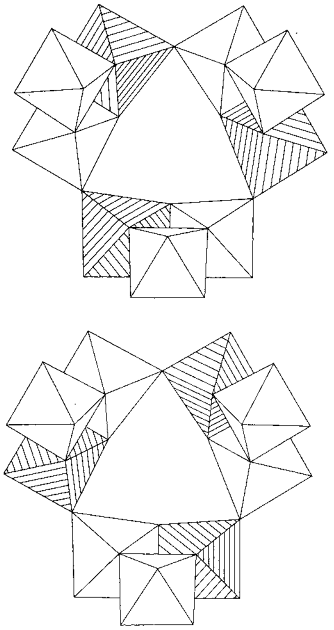

Figure 3. Polyhedral representation of the central part of $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{18-}$ (**1**) for both enantiomers in $CsK_{14}[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]\cdot 39H_2O$. Abundances of the enantiomers are 60% (upper) and 40% (lower).

The novel polyoxoanion **1** can be described as a cyclic trimer of Keggin ions (see Figure 2). Three $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ units which accommodate a Mn^{2+} ion each are linked through three Mn−O−W bridges. Therefore **1** is the first example of a trimeric silicotungstate. Anion **1** exhibits a 3-fold rotational axis corresponding to C_3 symmetry, which means that **1** is chiral (see Figure 3). The manganese ion in each Keggin subunit of **1** is unevenly (0.6/0.4) disordered over two edge-shared octahedral positions adjacent to the W_3 unit rotated by $\pi/3$ (see Figure 1). This means that both enantiomers of **1** were present in a ratio of 3:2 in the crystal studied. Bond lengths and angles of **1** do not show unusual features, but interpretation is limited for the disordered metal atom sites. The Mn−O−W angle between adjacent Keggin units in **1** is 145(1)°. The charge of **1** is 15− based on the number of cations (Cs^+, K^+) identified by X-ray crystallography and elemental analysis. This means that each of the three Keggin subunits of **1** is monoprotonated. However, bond-valence sum calculations[19] are not conclusive with respect to the site of protonation, most likely as a result of manganese disorder.

Interestingly **1** is formed by interaction of the dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with Mn^{2+} ions in acidic medium at room temperature. Anion **1** consists of three monosubstituted $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ Keggin fragments, which indicates that the mechanism of formation of **1** must involve insertion of Mn^{2+}, isomerization ($\gamma \rightarrow \beta$), gain of tungsten, and trimerization. However, details and the sequence of the above steps remain unclear. Most likely monomeric $[\beta_2\text{-}SiW_{11}MnO_{39}(H_2O)]^{6-}$ is

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the principal reaction product in solution. Since this species is chiral it can be expected that both enantiomers, (+)-$[\beta_2\text{-SiW}_{11}\text{MnO}_{39}(\text{H}_2\text{O})]^{6-}$ and (−)-$[\beta_2\text{-SiW}_{11}\text{MnO}_{39}(\text{H}_2\text{O})]^{6-}$, are present in equal amounts. Condensation of monomeric units is presumably initiated by crystallization. It is interesting that cyclic trimers are formed rather than a linear-chain polymer as observed for $[(\text{SiW}_{11}\text{CuO}_{39})_n]^{6n-}$, $[(\text{XW}_{11}\text{CoO}_{39})_n]^{5n-}$ (X = P, As), and $[(\text{PM}_{11}\text{MnO}_{39})_n]^{5n-}$ (M = W, Mo).[20−22] These compounds consist of α-Keggin units with the transition metal being disordered over two positions on opposite ends of the Keggin ion. The first condensation step during formation of **1** requires interaction of the terminal water molecule on the Mn^{2+} ion of a $[\beta_2\text{-SiW}_{11}\text{MnO}_{39}(\text{H}_2\text{O})]^{6-}$ ion with a terminal oxo group of another substituted Keggin ion. This terminal oxo group must be the one of the unique tungsten atoms in the same triad as the Mn^{2+} ion and adjacent to the W_3 unit rotated by $\pi/3$. Furthermore the second Keggin ion must be the same enantiomer as the first, e.g., (+,+) or (−,−). The second condensation step involves interaction of this dimeric unit with a third Keggin ion of the same enantiomeric type leading to ring closure. The two enantiomers formed could be represented as (+,+,+)**1** and (−,−,−)**1**, respectively. Apparently the conformation of the chiral dimer is crucial for the formation of cyclic **1**. The observed enantiomeric excess of the title compound in the solid state is most likely a property of the single crystal studied rather than the bulk solid.

It can also be helpful to compare the synthetic conditions of **1** with those used for the syntheses of $[\gamma\text{-SiMn}_2\text{W}_{10}\text{O}_{38}(\text{H}_2\text{O})_2]^{8-}$ (**2**) and $[\{\alpha\text{-SiMn}_2\text{W}_9\text{O}_{34}(\text{H}_2\text{O})\}_2]^{12-}$ (**3**) which were reported by Zhang et al.[10] and Kortz et al.,[16] respectively. All three anions **1**, **2**, and **3** were synthesized in aqueous solution by interaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with Mn^{2+} ions. Synthesis of **3** was performed by reacting $\text{MnCl}_2\cdot2\text{H}_2\text{O}$ and $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ in a 1.0 M sodium acetate buffer (pH 4.8) at 90 °C for 40 min. On the other hand no heating was needed for the syntheses of **1** and **2**. Anion **2** was synthesized by addition of a solution of $\text{Mn(OAc)}_2\cdot2\text{H}_2\text{O}$ in water to an aqueous solution of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ at pH 3.9 (adjusted by acetic acid) and stirring for 5 min. Synthesis of **1** was performed by addition of solid $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ to an aqueous solution of $\text{MnCl}_2\cdot2\text{H}_2\text{O}$ (see Experimental Section). Then glacial acetic acid was added dropwise until pH 3.9, and the solution was stirred at room temperature for 15 min. It becomes apparent that the synthetic conditions for **1** and **2** are quite similar although their structures are very different. The most significant difference in the preparation of **1** and **2** appears to be the absolute concentration of the limiting reagent $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$, which was about 10 times larger for **2** than for **1**. However, it cannot be ruled out that the equilibrium constants for **1** and **2** also depend on the composition and concentration of spectator ions in addition to pH and concentration of reactants.

Furthermore it seems that isomerization of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ to $[\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-}$ during the synthesis of **1** is facile as a result of interaction with Mn^{2+} ions since there is no need for heating. This observation indicates that both steps of the transformation $[\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-} \rightarrow [\beta\text{-SiW}_{10}\text{O}_{37}]^{10-} \rightarrow [\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ are fully reversible in the presence of Mn^{2+} ions. It should be remembered that $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ is synthesized from $[\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-}$ in a one-step reaction according to Tézé et al.[9] Kortz et al. observed reversibility of the transformation $[\beta\text{-SiW}_{10}\text{O}_{37}]^{10-} \rightarrow [\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ for the synthesis of $[\{\beta\text{-SiNi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2(\text{H}_2\text{O})\}_2]^{12-}$ (**4**), which contains the $[\beta\text{-SiW}_{10}\text{O}_{37}]^{10-}$ fragment.[15] Anion **4** was formed by reacting $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with Ni^{2+} ions in a 0.5 M potassium acetate buffer (pH 4.8) at 50 °C for 45 min. Reversibility of the transformation $[\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-} \rightarrow [\beta\text{-SiW}_{10}\text{O}_{37}]^{10-}$ during the synthesis of **1** requires incorporation of tungsten, which means that some $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ must decompose during the course of the reaction. This is not unfeasible given the relatively low starting concentration of decatungstosilicate (7.5 mM).

Efforts to synthesize **1** by direct interaction of monolacunary $[\beta_2\text{-SiW}_{11}\text{O}_{39}]^{8-}$ with Mn^{2+} ions and attempts to separate the enantiomers (+,+,+)**1** and (−,−,−)**1** are in progress.

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Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) $\{\text{K}_6[\text{SiW}_{11}\text{CuO}_{39}]\cdot14\text{H}_2\text{O}\}_n$, $a = 23.592(6)$ Å, $b = 10.787(4)$ Å, $c = 18.809(5)$ Å, $V = 4786(3)$ Å^3, $T = -77$ °C, *Pnma*, $Z = 4$, Cu−O−W = 156(5)°. Dickman, M. H., private communication.

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